

WO 2008/145729 A1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



PCT

(43) International Publication Date  
4 December 2008 (04.12.2008)

(10) International Publication Number  
WO 2008/145729 A1

(51) International Patent Classification:  
*C07C 31/34* (2006.01)      *B01F 7/18* (2006.01)  
*B01F 3/04* (2006.01)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, IIN, IIR, IIU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SI, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number:  
PCT/EP2008/056688

(22) International Filing Date: 30 May 2008 (30.05.2008)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:

07109461.9      1 June 2007 (01.06.2007)      EP  
61/013,676      14 December 2007 (14.12.2007)      US

(71) Applicant (for all designated States except US): SOLVAY (SOCIETE ANONYME) [BE/BE]; Rue du Prince Albert, 33, B-1050 Bruxelles (BE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): BORREMANS, Daniel [BE/BE]; Rue Séraphin Anthoine, 32, B-6032 Mont-sur-Marchienne (BE).

(74) Agent: VANDE GUCHT, Anne; SOLVAY (Société Anonyme), Intellectual Property Department, Rue de Ransbeek, 310, B-1120 Bruxelles, (BE).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(54) Title: PROCESS FOR MANUFACTURING A CHLOROHYDRIN

(57) Abstract: Process for manufacturing a chlorohydrin. Process for manufacturing a chlorohydrin by reacting a poly hydroxylated - aliphatic hydrocarbon, an ester of a poly hydroxylated - aliphatic hydrocarbon, or a mixture thereof with a chlorinating agent in a reactor containing a liquid reaction medium wherein the chlorinating agent is used at least partially in the gaseous form, and wherein said reactor is stirred by means of a stirring system comprising at least one radial - flow impeller and at least one axial - flow impeller.

Process for manufacturing a chlorohydrin

The present patent application claims the benefit of the patent application EP 07109461.9 filed on 01 June 2007 and of the provisional US patent application 61/013676 filed on 14 December 2007, the content of both of which is incorporated here by reference.

5 The present invention relates to a process for preparing a chlorohydrin. It relates more specifically to a process for preparing a chlorohydrin in a stirred reactor.

10 Chlorohydrins are reaction intermediates in the preparation of epoxides and derived products. Dichloropropanol, for example, is a reaction intermediate in the preparation of epichlorohydrin and of epoxy resins (Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, 1992, Vol. 2, page 156, John Wiley & Sons, Inc.).

15 According to known processes it is possible to obtain dichloropropanol in particular by hypochlorinating allyl chloride, by chlorinating allyl alcohol and by hydrochlorinating glycerol. This latter process has the advantage that the dichloropropanol can be obtained starting from fossil raw materials or from renewable raw materials, and it is known that natural petrochemical resources, from which the fossil materials are obtained, such as petroleum, natural gas or coal, for example, are limited in their terrestrial availability.

20 Patent application WO 2005/021476 describes a process for preparing dichloropropanol by reacting glycerol with gaseous hydrogen chloride in a liquid-gas type reactor. The dispersing devices disclosed for dispersing gaseous hydrogen chloride are nozzles, perforated plates or pipes, microporous plates and ejectors. To be efficient, *i.e.* to produce fine gas bubbles, such systems must 25 present very small apertures which can easily be clogged either by insoluble matter in the liquid reaction medium or by corrosion products of the dispersion device by the corrosive gas.

The goal of the invention is to provide a process for manufacturing a chlorohydrin which does not suffer of such problems.

30 The invention is therefore related to a process for manufacturing a chlorohydrin by reacting a polyhydroxylated-aliphatic hydrocarbon, an ester of a polyhydroxylated-aliphatic hydrocarbon, or a mixture thereof with a chlorinating

- 2 -

agent in a reactor containing a liquid reaction medium wherein the chlorinating agent is used at least partially in the gaseous form, and wherein said reactor is stirred by means of a stirring system comprising at least one radial-flow impeller and at least one axial-flow impeller.

5 By impeller, one intends to designate one that impels, as a rotating device used to force a fluid in a desired direction under pressure. A flat disk is not considered as being an impeller.

10 The stirring system contains often one radial-flow impeller and two axial-flow impellers and frequently two radial-flow impellers and one axial-flow impeller.

15 It has surprisingly been found that with such a stirring system :

- a) a high dispersion of the gaseous chlorinating agent in the liquid reaction mixture can be obtained with no aperture size limitation to the gas injection system, thereby eliminating the risk of clogging problem of the injection device, and
- b) a good mixing can be obtained in the liquid reaction medium.

20 Without being bound by any theory, it is believed that the radial-flow impeller allows a very efficient dispersion of small gas bubbles in the liquid even at high gas flow rates, while the axial-flow impeller ensures the homogeneous distribution of the small gas bubbles throughout the liquid reaction medium and a good homogenization of the liquid reaction mixture itself.

25 An additional advantage is that simpler geometry of the gas injection system are suitable, which are easier to cover or to manufacture in materials resistant to the chlorinating agent.

30 A further additional advantage of such a stirring system is that it is able to handle high gas rates without flooding. Flooding is the condition where the mixing system is not in control of the flow pattern in the liquid, rather the gas is in control.

35 Another further advantage of such a stirring system is that it can provide a high dispersion of the gaseous chlorinating agent in the liquid reaction mixture without a shroud or draft tube, which confines the flow pattern. The use of baffles along the walls of the reactor does not constitute shrouding of the stirring system.

The term "polyhydroxylated aliphatic hydrocarbon" refers to a hydrocarbon which contains at least two hydroxyl groups attached to two

different saturated carbon atoms. The polyhydroxylated aliphatic hydrocarbon may contain, but is not limited to, from 2 to 60 carbon atoms.

Each of the carbons of a polyhydroxylated aliphatic hydrocarbon bearing the hydroxyl functional group (OH) cannot possess more than one OH group and must have sp<sub>3</sub> hybridization. The carbon atom carrying the OH group may be primary, secondary or tertiary. The polyhydroxylated aliphatic hydrocarbon used in the present invention must contain at least two sp<sub>3</sub>-hybridized carbon atoms carrying an OH group. The polyhydroxylated aliphatic hydrocarbon includes any hydrocarbon containing a vicinal diol (1,2-diol) or a vicinal triol (1,2,3-triol), including the higher, vicinal or contiguous orders of these repeating units. The definition of the polyhydroxylated aliphatic hydrocarbon also includes, for example, one or more 1,3-, 1,4-, 1,5- and 1,6-diol functional groups. The polyhydroxylated aliphatic hydrocarbon may also be a polymer such as polyvinyl alcohol. Geminal diols, for example, are excluded from this class of polyhydroxylated aliphatic hydrocarbons.

The polyhydroxylated aliphatic hydrocarbons may contain aromatic moieties or heteroatoms, including, for example, heteroatoms of halogen, sulphur, phosphorus, nitrogen, oxygen, silicon and boron type, and mixtures thereof.

Polyhydroxylated aliphatic hydrocarbons which can be used in the present invention comprise, for example, 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1-chloro-2,3-propanediol (chloropropanediol), 2-chloro-1,3-propanediol (chloropropanediol), 1,4-butanediol, 1,5-pentanediol, cyclohexanediols, 1,2-butanediol, 1,2-cyclohexanediethanol, 1,2,3-propanetriol (also known as "glycerol" or "glycerin"), and mixtures thereof. With preference the polyhydroxylated aliphatic hydrocarbon used in the present invention includes, for example, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, chloropropanediol and 1,2,3-propanetriol, and mixtures of at least two thereof. More preferably the polyhydroxylated aliphatic hydrocarbon used in the present invention includes, for example, 1,2-ethanediol, 1,2-propanediol, chloropropanediol and 1,2,3-propanetriol, and mixtures of at least two thereof. 1,2,3-Propanetriol or glycerol is the most preferred.

The esters of polyhydroxylated aliphatic hydrocarbon may be present in the polyhydroxylated aliphatic hydrocarbon and/or may be produced in the process for preparing the chlorohydrin and/or may be prepared prior to the

process for preparing the chlorohydrin. Examples of esters of the polyhydroxylated aliphatic hydrocarbon comprise ethylene glycol monoacetate, propanediol monoacetates, glycerol monoacetates, glycerol monostearates, glycerol diacetates and mixtures thereof.

5 The term "chlorohydrin" is used here in order to describe a compound containing at least one hydroxyl group and at least one chlorine atom attached to different saturated carbon atoms. A chlorohydrin which contains at least two hydroxyl groups is also a polyhydroxylated aliphatic hydrocarbon. Accordingly the starting material and the product of the reaction may each be chlorohydrins.

10 In that case the "product" chlorohydrin is more chlorinated than the starting chlorohydrin, in other words has more chlorine atoms and fewer hydroxyl groups than the starting chlorohydrin. Preferred chlorohydrins are chloroethanol, chloropropanol, chloropropanediol, dichloropropanol and mixtures of at least two thereof. Dichloropropanol is particularly preferred. Chlorohydrins which

15 are more particularly preferred are 2-chloroethanol, 1-chloropropan-2-ol, 2-chloropropan-1-ol, 1-chloropropane-2,3-diol, 2-chloropropane-1,3-diol, 1,3-dichloropropan-2-ol, 2,3-dichloropropan-1-ol and mixtures of at least two thereof.

20 The polyhydroxylated aliphatic hydrocarbon, the ester of polyhydroxylated aliphatic hydrocarbon, or the mixture thereof in the process according to the invention may be obtained starting from fossil raw materials or starting from renewable raw materials, preferably starting from renewable raw materials.

25 By fossil raw materials are meant materials obtained from the processing of petrochemical natural resources, such as petroleum, natural gas and coal, for example. Among these materials preference is given to organic compounds containing 2 and 3 carbon atoms. When the polyhydroxylated aliphatic hydrocarbon is glycerol, allyl chloride, allyl alcohol and "synthetic" glycerol are particularly preferred. By "synthetic" glycerol is meant a glycerol generally obtained from petrochemical resources. When the polyhydroxylated aliphatic

30 hydrocarbon is ethylene glycol, ethylene and "synthetic" ethylene glycol are particularly preferred. By "synthetic" ethylene glycol is meant an ethylene glycol generally obtained from petrochemical resources. When the polyhydroxylated aliphatic hydrocarbon is propylene glycol, propylene and "synthetic" propylene glycol are particularly preferred. By "synthetic"

35 propylene glycol is meant a propylene glycol generally obtained from petrochemical resources.

By renewable raw materials are meant materials obtained from the processing of renewable natural resources. Among these materials preference is given to "natural" ethylene glycol, "natural" propylene glycol and "natural" glycerol. "Natural" ethylene glycol, propylene glycol and glycerol are obtained 5 for example by conversion of sugars by thermochemical processes, it being possible for these sugars to be obtained starting from biomass, as described in "Industrial Bioproducts : Today and Tomorrow", Energetics, Incorporated for the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of the Biomass Program, July 2003, pages 49, 52 to 56. One of 10 these processes is, for example, the catalytic hydrogenolysis of sorbitol obtained by thermochemical conversion of glucose. Another process is, for example, the catalytic hydrogenolysis of xylitol obtained by hydrogenation of xylose. The xylose may for example be obtained by hydrolysis of the hemicellulose present in maize fibres. By "glycerol obtained from renewable raw materials" is meant, 15 in particular, glycerol obtained during the production of biodiesel or else glycerol obtained during conversions of animal or vegetable oils or fats in general, such as saponification, transesterification or hydrolysis reactions.

Among the oils which can be used in the process of the invention, mention may be made of all common oils, such as palm oil, palm kernel oil, copra oil, 20 babassu oil, former or new (low erucic acid) colza oil, sunflower oil, maize oil, castor oil and cotton oil, peanut oil, soya bean oil, linseed oil and crambe oil, and all oils obtained, for example, from sunflower plants or colza plants obtained by genetic modification or hybridization.

It is also possible to employ used frying oils, various animal oils, such as 25 fish oils, tallow, lard and even squaring greases.

Among the oils used mention may also be made of oils which have been partly modified by means, for example, of polymerization or oligomerization, such as, for example, the "stand oils" of linseed oil and of sunflower oil, and blown vegetable oils.

30 A particularly suitable glycerol may be obtained during the conversion of animal fats. Another particularly suitable glycerol may be obtained during the production of biodiesel. A third, very suitable glycerol may be obtained during the conversion of animal or vegetable oils or fats by transesterification in the presence of a heterogeneous catalyst, as described in documents FR 2752242, 35 FR 2869612 and FR 2869613. More specifically, the heterogeneous catalyst is selected from mixed oxides of aluminium and zinc, mixed oxides of zinc and

titanium, mixed oxides of zinc, titanium and aluminium, and mixed oxides of bismuth and aluminium, and the heterogeneous catalyst is employed in the form of a fixed bed. This latter process can be a process for producing biodiesel.

5 The chlorination agent generally comprises hydrogen chloride as described in WO 2005/054167, from page 4, line 30 to page 6, line 2, the content of which is incorporated herein by reference.

10 In the process according to the invention, the chlorinating agent is used at least partially in the gaseous form. It is often used completely in the gaseous form. Frequently the chlorinating agent used is gaseous hydrogen chloride or a mixture of gaseous hydrogen chloride and of a solution of hydrogen chloride. The solution of hydrogen chloride is often an aqueous solution.

15 In the process according to the invention, the reaction between the polyhydroxylated-aliphatic hydrocarbon, the ester of the polyhydroxylated-aliphatic hydrocarbon, or the mixture thereof with the chlorinating agent can be carried out as described in Patent Applications WO 2005/054167, WO 2006/100311, WO 2006/100312, WO 2006/100313, WO 2006/100314, WO 2006/100315, WO 2006/100316, WO 2006/100317, WO 2006/106153, WO 2007/054505, WO 2006/100318, WO 2006/100319, WO 2006/100320, WO 2006/106154, WO 2006/106155, WO 2007/054505 and FR 06/05325, all filed in 20 the name of Solvay SA, and the contents of all of which are incorporated herein by reference.

25 Radial-flow impellers have blades which are generally parallel to the axis of the drive shaft. Non limitative examples of radial-flow impellers are notably :  
a) the turbine stirrer, such as the Rushton turbine comprising several flat blades on a disk (impeller (A) of figure 1), or such as the Smith turbine comprising several curved blades on a disk (impeller (G) on figure 1), which are advantageously high-speed stirrers that typically set the fluid in radial motion or, at higher viscosities, in tangential motion. This type of impellers are particularly effective with low-viscosity liquids and baffled vessels. For this 30 type of impellers, the diameter ratio D/d (D = reactor vessel diameter; d = stirrer diameter) ranges advantageously from 2 to 5. During rotation, the turbine stirrers cause typically high levels of shear and is generally well suited to dispersion processes;  
b) the impeller stirrer (impeller (B) of figure 1), which was notably developed 35 in the past for use in enamel-coated vessels, and thus has rounded stirring arms. It is generally used in conjunction with small clearances from the

bottom. For this type of impeller, the diameter ratio D/d ranges advantageously around 1.5 (that is to say between 1 and 2, preferably between 1.2 and 1.8), either with or without baffles. It can also operate with strongly fluctuating fill levels (e.g., during vessel discharging) because it is able to mix even small amounts of liquid;

- 5        c) the cross-beam impeller (impeller (C) of figure 1), the grid impeller (impeller (E) of figure 1), and the blade impeller (impeller (D) of figure 1), which advantageously belong to the group of low-speed stirrer types and are typically used with D/d from 1.5 to 2. They can operate with baffles or,
- 10        especially for viscous media, without, and are especially well suited to homogenization;
- 15        d) the low-speed anchor stirrer (impeller (F) of figure 1), which is generally operated at very small clearances from the wall, that is to say at diameter ratio D/d from 1.005 to 1.5, preferably from 1.005 to 1.05 and is particularly appropriate for enhancing heat transfer in highly viscous media;
- 20        e) the rotor-stator stirrer or stirrer operating on the rotor – stator principle (Figure 2), in which the rotor advantageously consists of a blade (1) or paddle stirrer (1) enclosed by a ring of baffles (stator) (2). As a result, high levels of shear are generally exerted on an extremely small volume;
- 25        f) the toothed disk (figure 4); using this stirrer, the liquid is advantageously accelerated radially in a thin ring away from the centre, and then quickly decelerated. High levels of shear can thus be achieved, even without a stator ring or baffles.

The radial-flow impeller is often chosen among the group consisting of a turbine stirrer, an impeller stirrer, a cross-beam impeller, a grid-impeller, a blade impeller, a low-speed anchor stirrer, a rotor-stator stirrer and a toothed disk. The radial-flow impeller is frequently chosen among the group consisting of a turbine stirrer, an impeller stirrer, a cross-beam impeller, a grid-impeller, a blade impeller.

- 30        The radial-flow impeller is more often a turbine stirrer, frequently a turbine stirrer of the Rushton type or a turbine stirrer of the Smith type, and more specifically a turbine stirrer of the Smith type. Such turbine comprises generally at least 2 curved blades on a disk and preferably at least 3 curved blades. The number of curved blades is generally of at most 10 and preferably of at most 8.
- 35        A turbine with 6 curved blades on a disk is the most preferred turbine stirrer of the Smith type. A turbine with 4 curved blades on a disk is also very well suited.

Without being bound by any theory, it is believed that another additional advantage of the curved blade radial-flow impeller selected is that it permits to insure a constant power draw when the gas flow rate varies inside a broad range. Under gassed conditions, this power draw is very close to the power draw 5 achieved when there is no gas injection and therefore it avoids the over sizing of the whole cinematic chain (including the motor, the reducer, the shaft and the mechanical seal) and allows considerable investment savings.

The curved blades can be of any form, preferably hemi-cylindrical, hemi-cylindrical more or less flattened, and parabolic, and more preferably parabolic.

10 The distances between two successive blades can be equal or different. The distances are preferably equal.

By reference with the disk plane, the curved blades can be symmetrical or asymmetrical, preferably asymmetrical.

15 In general, the asymmetric radial-flow impeller will include a plurality of generally radially extending blades. Each of the blades will include upper and lower sheet-like portions which meet at a vertex, such that the cross-section of the blade will be generally parabolic or u-shaped. The width of the upper portion of each blade will be longer than the width of the lower portion making the blade asymmetric. Thus, at the leading edge of the blade there will be an upper portion 20 overhang which can capture and disperse rising gas bubbles. The impeller can have any number of blades, but it is preferred that it has from 4 to 12 blades with 6 being most preferred. The upper sheet could extend 15 to 50 percent further than the width of the lower sheet, with about 25 percent being most preferred.

Axial-flow and mixed flow impellers include all impeller in which the 25 blade(s) make(s) an angle of less than 90° with the plane of rotation. Non limitative examples of said impellers are notably:

- a) the paddle stirrer with pitched blades (also known as pitched blade turbine) [impeller (H) of figure 1] and the propeller stirrer (also known as marine-type mixing propeller) [impeller (I) of figure 1], which typically belong to the 30 group of high-speed mixers that advantageously generate an axial flow pattern. They are advantageously well suited to homogenization and suspension of solids and are typically used with D/d from 2 to 3.
- b) multistage stirrers with pitched stirring surfaces such as the cross-beam stirrer with pitched beams [impeller (J) of figure 1] and the MIG stirrer 35 [impeller (K) of figure 1] and INTERMIG stirrer [impeller (L) of figure 1] of the Ekato company, Schopfheim, Germany, which are particularly suitable

for enhancing the axial flow and/or for high liquid level to diameter ratios ( $H/D > 1$ , wherein  $D$  = reactor vessel diameter;  $H$  = height of the liquid in the reactor vessel) are required. These stirrers are advantageously operated at low speeds. The diameter ratio for these stirrers  $D/d$  exceeds advantageously 5 1.5 when they are used in combination with baffles and is around 1.1 (that is to say between 1.005 and 1.5) when they are used without baffles.

- c) the low-speed helical ribbon stirrer [impeller (M) of figure 1], which is generally used with small wall clearances ( $D/d > 1.05$ ) and typically operated in such a way that it drives the liquid downwards along the wall;
- 10 d) the hollow stirrer (figure 3), which typically has a hollow head and is connected through a hollow shaft to the gas-filled space above the liquid medium, and which is thus generally suitable for supplying a gas to a liquid; the suction generated behind the stirrer edges during rotation can be advantageously used to supply a gas in the reaction vessel;
- 15 e) the turbofoil impeller [impeller (N) of figure 1].

The axial-flow impeller is often chosen among the group consisting of a paddle-stirrer with pitched blades, a propeller stirrer (marine-type mixing propeller), a cross-beam stirrer with pitched beams, a MIG stirrer, an INTERMIG stirrer, a low-speed helical ribbon stirrer, a turbofoil impeller and a 20 hollow stirrer.

The axial-flow impeller is frequently chosen among the group consisting of a paddle-stirrer with pitched blades, a propeller stirrer (marine-type mixing propeller), a MIG stirrer, an INTERMIG stirrer and a turbofoil impeller.

The axial-flow impeller is more often chosen among the group consisting 25 of a paddle-stirrer with pitched blades, a propeller stirrer (marine-type mixing propeller) and a turbofoil impeller. The axial-flow impeller is more specifically a paddle-stirrer with pitched blades or a turbofoil impeller, and more particularly a turbofoil impeller.

The number of blades is generally higher than or equal to 2 and preferably 30 higher than or equal to 3. That number is usually lower than or equal to 8 and preferably lower than or equal to 6. A number of 4 blades is particularly well suited.

The angle the blade(s) make(s) with the plane of rotation is preferably 35 lower than or equal to  $60^\circ$ , more preferably lower than or equal to  $55^\circ$  and most preferably lower than or equal to  $50^\circ$ . That angle is generally higher than or

equal to 30°, preferably higher than or equal to 35°, and more preferably higher than or equal to 40°. An angle of 45° is particularly well suited.

Hydrofoils impellers are a very important class of pitched blade turbines combining a bigger pumping capacity with a reduced power consumption. These 5 performances are obtained by an optimized blade profile. Basically the angle of the trailing edge of the blade with the horizontal plane changes with the distance from the shaft like in an airplane propeller. In practice this angle change can be continuous or discontinuous. This allows a nearly uniform flow pattern at the discharge of the impeller and reduces the eddies at the trailing edge. Examples of 10 hydrofoil impellers are Lightnin A 310, A 320 and A 340, Chemineer HE3, Philadelphia Mixers MHS & LS impellers, Pfaudler TBF, Mixel TT, TTP and TTF.

The distances between two successive blades can be equal or different. The distances are preferably equal.

15 The sides of the blades can independently be flat, curved or faceted. A flat bottom oriented side and a two faceted top oriented side is more preferred.

Examples of such impellers are the pitched blade turbine (impeller (H), Figure 1) and the turbofoil (impeller (N), Figure 1). The turbofoil is the most preferred axial-flow impeller. It offers the additional advantage to be more 20 easily coated, especially when glass-lined or enamelled coating is required.

In the stirring system of the process of the invention, the radial-flow impeller and the axial-flow impeller can be placed on a same shaft or on a different shaft. It is preferred that the radial-flow impeller and the axial-flow impeller are placed on a same shaft.

25 The stirring system of the invention can be placed in any position in the reactor, vertically, horizontally or obliquely, preferably vertically.

In the stirring system of the invention, the axial-flow impeller provides a flow of the liquid reaction medium which generally can be downwardly or upwardly, and is frequently downwardly.

30 In the stirring system of the process of the invention, the radial-flow impeller can be placed below or above the axial-flow impeller. It is preferred that the radial-flow impeller is placed below the axial-flow impeller. The diameter of the radial-flow impeller and of the axial-flow impeller depends on the reactor diameter.

35 The diameter of the radial-flow impeller is generally higher than or equal to one 33% of the reactor diameter, often higher than or equal to 40% of the

reactor diameter and frequently higher than or equal to 50% of the reactor diameter. The diameter of the radial-flow impeller is generally lower than or equal to 70% of the reactor diameter, often lower than or equal to 65% of the reactor diameter and frequently lower than or equal to 55% of the reactor diameter.

5 diameter.

The diameter of the axial-flow impeller is generally higher than or equal to 33% of the reactor diameter, often higher than or equal to 40% of the reactor diameter and frequently higher than or equal to 50% of the reactor diameter. The diameter of the axial-flow impeller is generally lower than or equal to 70% of the reactor diameter, often lower than or equal to 65% of the reactor diameter and frequently lower than or equal to 55% of the reactor diameter.

10 Those impeller diameter are measured between two opposite points on the outer periphery of the impeller.

15 The reactor diameter is the internal diameter of the reactor possibly diminished of the size of possibly present baffles.

The diameter of the radial-flow impeller and of the axial-flow impeller can be equal or different. When they are different, the diameter of the radial-flow impeller can be higher than or lower than the diameter of the axial-flow impeller. The diameter of the radial-flow impeller is often higher than the diameter of the axial-flow impeller. The diameter of the radial-flow impeller and of the axial-flow impeller are frequently equal.

20 The distance between the radial-flow impeller and the axial-flow impeller depends on the reactor height and on the impeller diameter.

25 When the radial-flow impeller and the axial-flow impeller have the same diameter, that distance is generally higher than or equal to one quarter of the impeller diameter, preferably higher than or equal to one third of the impeller diameter and more preferably higher than or equal to one half of that diameter. That distance is generally lower than or equal to two times the impeller diameter, and preferably lower than or equal to 1.5 times the impeller diameter. A distance 30 equal to the impeller diameter is particularly well suited.

35 When the radial-flow impeller and the axial-flow impeller do not have the same diameter, that distance is generally higher than or equal to one quarter of the impeller highest diameter, preferably higher than or equal to one third of that impeller diameter and more preferably higher than or equal to one half of that diameter. That distance is generally lower than or equal to two times the impeller highest diameter, and preferably lower than or equal to 1.5 times the

impeller diameter. A distance equal to the impeller diameter is particularly well suited.

5 In the process according to the invention, the stirring system may contain one radial-flow impeller and two axial-flow impellers or two radial-flow impellers and one axial flow impeller.

10 When the stirring system contains one radial-flow impeller and two axial-flow impellers, the axial-flow impellers can be different or identical. They are often identical. For that stirring system, the impellers are often placed on a same shaft and the radial-flow impeller is frequently placed below the two axial-flow impellers.

15 When the stirring system contains two radial-flow impellers and one axial-flow impeller, the radial-flow impellers can be different or identical. They are often identical. For that stirring system, the impellers are often placed on a same shaft and the radial-flow impellers are frequently placed below the axial-flow impeller.

In the process according to the invention, the chlorination agent can be injected anywhere in the reactor with respect to the radial- and/or axial flow impellers.

20 When the stirring system contains one radial-flow impeller and one axial flow impeller, the radial-flow impeller being located below the axial-flow impeller, the chlorination agent is injected generally below the level of the radial-flow impeller, often at the level of the radial-flow impeller and sometimes between the levels of the radial- and axial flow impellers.

25 When the stirring system contains one radial-flow impeller and two axial flow impellers, the radial-flow impeller being located below the axial-flow impellers, the chlorination agent is injected generally below the level of the lowest radial-flow impeller, often at the level of the radial-flow impeller and sometimes between the levels of the radial- and the lowest axial flow impeller.

30 When the stirring system contains two radial-flow impellers and one axial flow impeller, the radial-flow impellers being located below the axial-flow impeller, the chlorination agent is injected generally below the level of the lowest radial-flow impeller, often at the level of the lowest radial-flow impeller, sometimes between the levels of the radial-flow impellers, usually at the level of the highest radial-flow impeller, and commonly between the levels of the highest radial-flow impeller and the axial flow impeller.

In the process according to the invention, the injection of the chlorination agent in the reactor can be a single point injection or a multiple points injection.

A preferred single point injection level below the level of the lowest radial-flow impeller is more frequently used.

5 The injection of the chlorination agent can be carried out by any means, like thorough a perforated ring or a central tube. The injection is often carried out by a central tube.

10 A diagrammatic, sectional front elevation view of a reactor containing a stirring system in accordance with the process of the invention, is presented at Figure 5, where (1) is a shaft, (2) are axial-flow impellers, (3) is a radial-flow impeller, (4) is the reactor, (5) is the shaft's axis and (6) is a pipe for injecting the chlorinating agent.

15 The speed of rotation of the stirring system will be set as a function of the stirring system type and reaction vessel diameter according to good practices well-known to the skilled in the art.

It will be generally preferred that the energy density obtained with the stirring system is of advantageously at least 0.5 kW/m<sup>3</sup> of liquid reaction medium, preferably at least 1 kW/m<sup>3</sup>, more preferably at least 1.2 kW/m<sup>3</sup>.

20 In general the energy density obtained with the stirring system is of advantageously at most 2 kW/m<sup>3</sup> of liquid reaction medium, preferably at most 1.5 kW/m<sup>3</sup>, more preferably at most 1.3 kW/m<sup>3</sup>.

25 The speed of rotation of the stirring device can vary in a broad domain; generally, the speed of rotation is of advantageously at least 30 rpm, preferably of at least 50 rpm, more preferably of at least 70 rpm and is of advantageously at most 350 rpm, preferably of at most 300 rpm, more preferably of at most 250 rpm.

In particular, for a reactor having a diameter of from 1000 to 4000 mm, the speed of rotation of the impeller is advantageously selected between 50 and 200 rpm.

30 In the process according to the invention, the stirring system can be made of any material. That system is preferably made of or covered with materials which are resistant to the chlorinating agent, under the conditions of reaction.

35 The materials that are resistant, under the conditions of reaction, to the chlorinating agent, are selected from enamelled steel, polymers, coatings by means of resins, metals or alloys, ceramics and metalloceramics, refractory materials and graphite.

These materials are such as described in the patent applications WO2005/054167 and WO2006/100317 of SOLVAY SA, the contents of which are incorporated herein by reference.

The polymers can be selected from polyolefins, fluorinated polymers and polymers containing sulphur. The polyolefins are often selected from polyethylene and polypropylene. Polypropylene is preferred. The fluorinated polymers are frequently selected from polytetrafluoroethylene, poly(vinylidene fluoride) and poly(perfluorovinylether). Polytetrafluoroethylene, and poly(perfluorovinylether) are more frequently used. The polymers containing sulphur are often selected from polysulfones and polysulfides, aromatic or aliphatic. Aromatic polysulfones or polysulfides are more often used.

The coating by resins are often coatings by epoxy or phenolic resins, frequently coating by phenolic resins.

The metals are generally selected from tantalum, titanium, nickel, copper, gold, silver and molybdenum, often selected from tantalum, nickel, copper, gold, silver and molybdenum, frequently selected from tantalum, gold, silver and molybdenum, more frequently selected from tantalum and molybdenum. Tantalum is a particularly convenient metal.

The alloys are usually selected from alloys containing nickel and molybdenum. Hastelloy B is a convenient nickel-molybdenum alloy.

Graphite generally can be non-impregnated or impregnated graphite. Impregnated graphite is particularly convenient. Graphite can be impregnated with any material like for instance polytetrafluoroethylene or phenolic resins.

The preferred material for the stirring system is enamelled or glass-lined steel.

The invention is also related to a stirring system comprising at least one radial-flow impeller and one axial-flow impeller. The stirring system exhibits the characteristics described hereabove.

The invention is finally related to the use of a stirring system comprising at least one radial-flow impeller and one axial-flow impeller for dispersing a gas in a liquid.

The examples below are intended to illustrate the invention, but without imposing any limitation theron.

Example 1 (in accordance with the invention)

A vessel with a diameter T of 3000 mm, a total height of 9200 mm (including top and bottom decimal heads) and a height of the cylindrical part of

8000 mm is equipped with a stirring system comprising one radial-flow impeller of the Rushton type comprising six flat blades and having a diameter  $D_R$  of 1500 mm, and one axial-flow impeller of the turbofoil type comprising four blades and having a diameter of  $D_A$  1500 mm. Both impellers are placed on the 5 same shaft. The radial flow impeller is placed below the axial flow impeller. The stirring system is placed vertically in the reactor as presented in Figure 5. The distance between the axial flow impeller and the top of the liquid is sufficient to avoid a vortex.

10 The vessel is filled with 33 m<sup>3</sup> of a liquid having a density of 1000 kg/m<sup>3</sup> and a viscosity of 2 cp. A gas with a density of 2.5 kg/m<sup>3</sup> is injected at a flow rate  $Q_g$  of 2000 kg/h (0.222 m<sup>3</sup>/s) in the liquid below the radial flow impeller.

We can calculate, for the stirring system, the following quantities :

1. the flooding speed ( $N_f$ ) which is the minimal speed to avoid flooding
2. the complete dispersion speed ( $N_{cd}$ ) which is the minimal speed to achieve 15 complete dispersion of the gas
3. the actual speed ( $N$ ) which is the nearest speed above the complete dispersion speed according to the American Gear Manufacturers Association
4. the power draw at actual speed under no gas conditions for the radial-flow impeller ( $P_u$ )<sub>R</sub>
5. the minimal motor power ( $P_{mu}$ )<sub>R</sub> at actual speed under no gas conditions for 20 the radial-flow impeller
6. the actual motor power at actual speed for the radial-flow impeller ( $P_m$ )<sub>R</sub>
7. the power draw at actual speed under gas conditions for the radial-flow impeller ( $P_g$ )<sub>R</sub>
8. the power draw at actual speed under no gas conditions for the axial-flow impeller ( $P_u$ )<sub>A</sub>
9. the minimal motor power at actual speed under no gas conditions for the 25 radial-flow and the axial-flow impellers ( $P_{mu}$ )<sub>RA</sub>
10. the actual motor power at actual speed for the radial-flow and axial-flow impellers ( $P_m$ )<sub>RA</sub>

30 using the following equations :

1.  $N_f = (Q_g * 9.81 * ((T/D_R)^{3.5}) / (30 * (D_R^4)))^{0.3333}$  where  $N_f$  is the flooding speed (sec<sup>-1</sup>) and  $Q_g$  is the volumetric gas flow rate (m<sup>3</sup>/sec), for the Rushton radial-flow impeller
2.  $N_{cd} = (Q_g * ((T * 9.81 / D_R)^{0.5}) / (0.2 * (D_R^{3.5})))^{0.5}$  where  $N_{cd}$  is the complete dispersion speed (sec<sup>-1</sup>)

- 16 -

3.  $(P_u)_R = Npo * \rho * (N^3) * (D_R^5)$  where  $Npo$  is the power number of the impeller (given by manufacturer and most of the time accessible in open literature: 5.5 for a Rushton turbine of 1500 mm of diameter),  $N$  is the actual impeller speed ( $\text{sec}^{-1}$ ),  $\rho$  is the liquid density ( $\text{kg/m}^3$ ) and  $(P_u)_R$  is the absorbed power (W)
- 5 4.  $(P_m)_R = 1.2 (P_u)_R$
- 5 5.  $(P_g)_R = 0.7 (P_u)_R$  for a gassing number  $F_1$  and another adimensional number  $F_{13-3}$  such that  $F_{13-3} < F_1 < 0.1$  where
  - a.  $F_1 = Qg / (N * (D_R^3))$
  - b.  $F_{13-3} = 0.0038 * ((T/D_R)^{0.5}) * ((Re^2)/Fr)^{0.07}$  where
    - 10 i.  $Re = N * D_R^2 * \rho / \mu$  is the Reynolds number with  $\mu$  is the liquid viscosity ( $\text{Pa} * \text{sec}$ )
    - ii.  $Fr = (D_R * N^2) / 9.81$  is the Froude number
6.  $(P_u)_A = Npo * \rho * (N^3) * (D_A^5)$  where  $Npo$  is the power number of the impeller (given by manufacturer and most of the time accessible in open literature: 0.38 for a turbofoil impeller of 1500 mm of diameter),  $N$  is the actual impeller speed ( $\text{sec}^{-1}$ ),  $\rho$  is the liquid density ( $\text{kg/m}^3$ ) and  $(P_u)_A$  is the absorbed power (W)
- 15 7.  $(P_u)_{RA} = (P_u)_R + (P_u)_A$
8.  $(P_m)_{RA} = 1.2 (P_u)_{RA}$
- 20 20. The results of the calculations are summarized in Table 1.

Example 2 (in accordance with the invention)

The conditions are identical to those of example 1 except that the radial-flow impeller is of the Smith type and comprises six asymmetric parabolic curved blades and the equations used are :

- 25 1.  $Nf = (Qg * 9.81 * ((T/D_R)^{3.5}) / (70 * (D_R^4)))^{0.3333}$  where  $Nf$  is the flooding speed ( $\text{sec}^{-1}$ ) and  $Qg$  is the volumetric gas flow rate ( $\text{m}^3/\text{sec}$ ), for the Smith radial-flow impeller
2.  $Ncd = (Qg * ((T * 9.81 / D_R)^{0.5}) / (0.4 * (D_R^{3.5})))^{0.5}$  where  $Ncd$  is the complete dispersion speed ( $\text{sec}^{-1}$ )
- 30 30. and  $Npo = 2.3$  for a Smith turbine.

The results of the calculations are summarized in Table 1.

Table 1

	Rushton/Turbofoil	Smith/Turbofoil	
	Exemple 1	Exemple 2	
Nf (rpm)	32.7	24.7	24.7
Ncd (rpm)	65.4	46.3	46.3
N (rpm)	68	68	56
(Pu) <sub>R</sub> (kW)	60.8	25.4	14.2
(Pmu) <sub>R</sub> (kW)	73.0	30.5	17.0
(Pm) <sub>R</sub> (kW)	75.0	37.0	18.5
(Pg) <sub>R</sub> (kW)	42.6	22.9	12.8
(Pu) <sub>A</sub> (kW)	4.2	4.2	2.4
(Pmu) <sub>RA</sub> (kW)	78.0	35.5	19.9
(Pm) <sub>RA</sub> (kW)	90	37	22

Example 3 (in accordance with the invention)

The conditions are identical to those of example 1 except that two radial flow impellers of the Rushton type having an equal diameter  $D_R$  of 1500 mm and an axial flow impeller of the turbofoil type having a diameter  $D_A$  of 1500 mm are used. The three impellers are placed on the same shaft. The radial flow impellers are placed below the axial flow impeller. The stirring system is placed vertically in the reactor. The distance between the axial flow impeller and the top of the liquid is sufficient to avoid a vortex.

The gas flowrate is split equally between the two radial flow impellers (1000 kg/ hr for each) and the gas is injected in the liquid below each radial flow impeller.

The results of the calculations are summarized in Table 2.

Table 2

Nf (rpm)	26
Ncd (rpm)	46.3
N (rpm)	56
(Pu) <sub>R</sub> (kW)	68
(Pmu) <sub>R</sub> (kW)	82
(Pm) <sub>R</sub> (kW)	90.0
(Pg) <sub>R</sub> (kW)	61
(Pu) <sub>A</sub> (kW)	2.4
(Pmu) <sub>RA</sub> (kW)	84.5
(Pm) <sub>RA</sub> (kW)	90

Example 4 (in accordance with the invention)

The conditions are identical to those of example 3 except that two radial flow impellers of the Smith type as in example 2 are used. The results of the calculations are summarized in Table 3.

5 Table 3

Nf (rpm)	20
Ncd (rpm)	32.7
N (rpm)	37
(Pu) <sub>R</sub> (kW)	8.2
(Pmu) <sub>R</sub> (kW)	9.8.
(Pm) <sub>R</sub> (kW)	11.0
(Pg) <sub>R</sub> (kW)	7.4
(Pu) <sub>A</sub> (kW)	0.7
(Pmu) <sub>RA</sub> (kW)	10.7
(Pm) <sub>RA</sub> (kW)	11

Example 5 (not in accordance with the invention)

The conditions of example 1 have been used except that a single axial flow impeller, *i.e.* a pitch blade turbine comprising four flat blades with the blades making an angle of 45° with the plane of rotation is used. The diameter of the axial flow impeller D<sub>A</sub> is 1500 mm. No radial flow impeller is present. The stirring system is placed vertically in the reactor. The distance between the axial flow impeller and the top of the liquid is sufficient to avoid a vortex. The gas is injected below the axial-flow impeller.

For this type of axial flow impeller pumping downward, we have:

$$15 \quad Nf = 11.7 * (Qg)^{0.5} / (D_R)^{1.63}$$

$$Nf = Ncd$$

The results of the calculations are summarized in Table 4.

Table 4

Nf (rpm)	120
Ncd (rpm)	120
N (rpm)	125
(Pu) <sub>A</sub> (kW)	110
(Pmu) <sub>RA</sub> (kW)	132
(Pm) <sub>RA</sub> (kW)	132

C L A I M S

- 1 Process for manufacturing a chlorohydrin by reacting a polyhydroxylated-aliphatic hydrocarbon, an ester of a polyhydroxylated-aliphatic hydrocarbon, or a mixture thereof with a chlorinating agent in a reactor containing a liquid reaction medium wherein the chlorinating agent is used at least partially in the gaseous form, and wherein said reactor is stirred by means of a stirring system comprising at least one radial-flow impeller and at least one axial-flow impeller.  
5
- 2 Process according to claim 1, wherein the radial-flow impeller is chosen among the group consisting of a turbine stirrer, an impeller stirrer, a cross-beam impeller, a grid-impeller, a blade impeller, a low-speed anchor stirrer, a rotor-stator stirrer and a toothed disk.  
10
- 3 Process according to claim 1 or 2 wherein the axial-flow impeller is chosen among the group consisting of a paddle-stirrer, a propeller stirrer (marine-type mixing propeller), a multi-stage stirrer with pitched stirring surface, a MIG stirrer, an INTERMIG stirrer, a low-speed helical ribbon stirrer, a  
15 turbofoil impeller and a hollow stirrer.
- 4 Process according to claim 2, wherein the radial-flow impeller is a turbine stirrer of the Smith type comprising from two to ten curved blades on a disk.  
20
- 5 Process according to claim 3, wherein the axial-flow impeller is a paddle stirrer or a turbofoil impeller comprising from two to eight blades making an angle from 30 to 60° with the plane of rotation.
- 6 Process according to claim 4, wherein the curved blades of the turbine  
25 stirrer are of hemicylindrical or parabolic form and asymmetrical by reference with the disk plane.
- 7 Process according to any of claims 1 to 6, wherein the radial-flow impeller and the axial-flow impeller are placed on a same shaft.
- 8 Process according to any of claims 1 to 7, wherein the radial-flow  
30 impeller is located below the axial flow impeller.

- 20 -

9 Process according to any of claims 1 to 8, wherein the axial-flow impeller provides a flow of the liquid reaction medium downwardly.

10 Process according to any of claims 1 to 9 wherein the stirring system is made of or covered with materials which are resistant to the chlorinating agent,  
5 under the conditions of reaction.

11 Process according to claim 10 wherein the materials that are resistant, under the conditions of reaction, to the chlorinating agent, are selected from enamelled (glass-lined) steel, polymers, coatings by means of resins, metals or alloys, ceramics and metalloceramics, refractory materials and graphite

10 12 Process according to any of claims 1 to 11, wherein two axial-flow impellers and one radial flow-impeller are located on a same shaft, the two axial-flow impellers being located above the radial-flow impeller.

13 Process according to any of claims 1 to 11, wherein one axial-flow impeller and two radial-flow impellers are located on a same shaft, the axial-flow  
15 impeller being located above the radial-flow impellers.

14 Process according to any of claims 1 to 13, wherein the chlorinating agent is injected in the reactor below the radial-flow impeller.

15 Process according to any of claims 1 to 14, wherein the chlorinating agent comprises hydrogen chloride.

Fig. 1

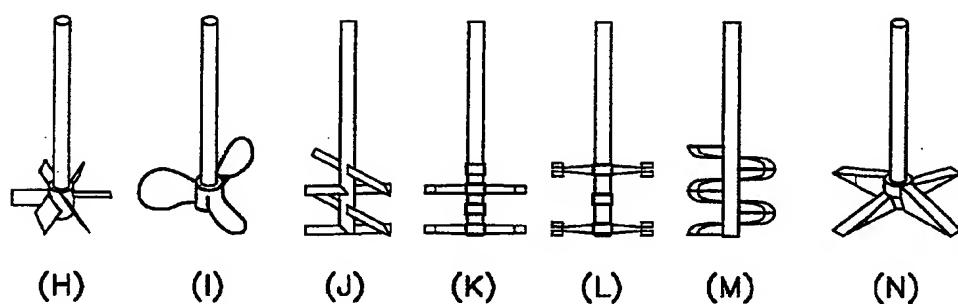
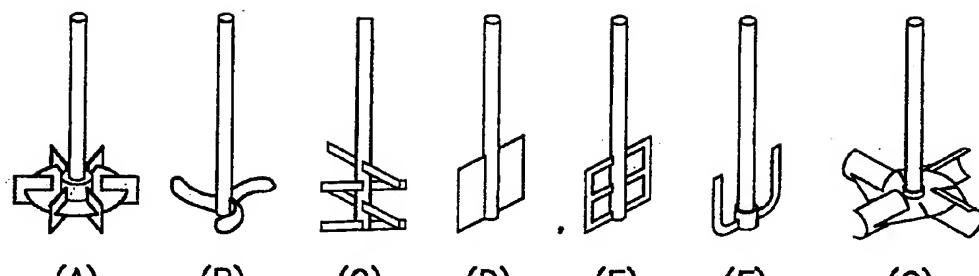


Fig. 2

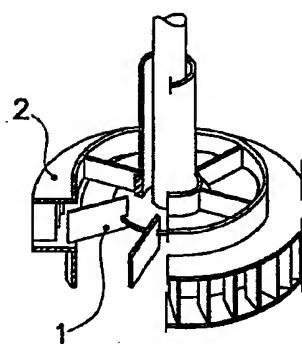


Fig. 3

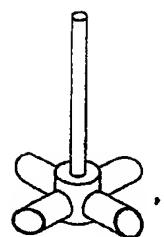
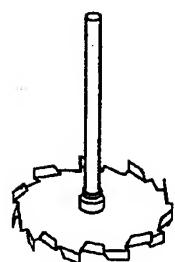
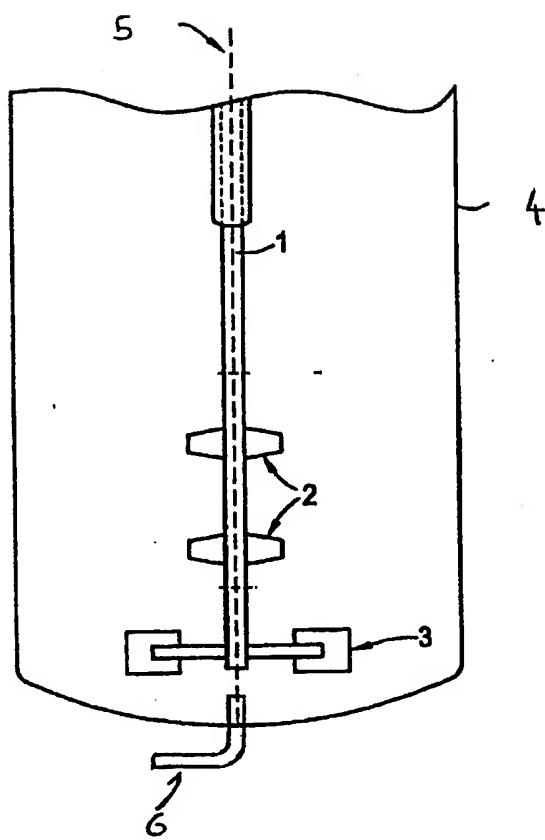


Fig. 4



**Fig. 5**

# INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/056688

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C07C31/34 B01F3/04 B01F7/18

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**C07C B01F**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**EPO-Internal, WPI Data**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2005/021476 A (SPOLEK [CZ]; KUBICEK PAVEL [CZ]; SLADEK PETR [CZ]; BURICOVA IVANA [CZ]) 10 March 2005 (2005-03-10) cited in the application page 5, lines 4-6; examples, e.g. Example 1 and Table 1; claims	1-15
Y	DE 37 21 003 C1 (SOLVAY WERKE GMBH) 1 December 1988 (1988-12-01) examples, e.g. Example 1; claims	1-15
Y	US 6 142 458 A (HOWK RICHARD A [US]) 7 November 2000 (2000-11-07) column 1, lines 4-12; claims	1-15
Y	EP 0 347 618 A (GEN SIGNAL CORP [US]) 27 December 1989 (1989-12-27) claims; Figures, e.g. Fig. 1A-1C, 2A and 2B;	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

23 October 2008

Date of mailing of the international search report

30/10/2008

Name and mailing address of the ISA/  
 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040.  
 Fax: (+31-70) 340-3016

Authorized officer

Sen, Alina

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/EP2008/056688

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 2005021476	A	10-03-2005	BR PI0413914 A CA 2537131 A1 CN 1845888 A CZ 20032346 A3 EP 1663924 A1 MX PA06002351 A UA 81971 C2 US 2007167659 A1		24-10-2006 10-03-2005 11-10-2006 13-04-2005 07-06-2006 31-08-2006 25-02-2008 19-07-2007
DE 3721003	C1	01-12-1988	NONE		
US 6142458	A	07-11-2000	NONE		
EP 0347618	A	27-12-1989	AU 607386 B2 AU 3515289 A BR 8906965 A CA 1290746 C DE 68915059 D1 DE 68915059 T2 DK 272589 A IE 64111 B1 NO 892314 A WO 8912496 A1 US 4882098 A ZA 8903885 A		28-02-1991 21-12-1989 11-12-1990 15-10-1991 09-06-1994 03-11-1994 21-12-1989 12-07-1995 21-12-1989 28-12-1989 21-11-1989 30-05-1990